Adsorption of Surface-Modified Colloidal Gold Particles onto Self-Assembled Monolayers: A Model System for the Study of Interactions of Colloidal Particles and Organic Surfaces

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Self-assembled monolayers (SAMs) were formed from ω-substituted alkanethiols, namely (1-mercaptoundec-11-yl)hexa(ethylene glycol) ($HS(CH_2)_{11}(OCH_2CH_2)_6OH$) and 1-dodecanethiol ($HS(CH_2)_{11}CH_3$), on the surface of planar gold films and on colloidal gold particles. A quantitative method for studying the physical adsorption of SAM-modified gold colloids onto the planar SAMs was developed. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to measure the composition of planar SAMs and to quantify the extent of colloidal adsorption, respectively. Results confirm that the colloids studied adsorb from the aqueous solution more extensively to hydrophobic surfaces, that the extent of adsorption increases with particle hydrophobicity, and that oligo(ethylene glycol) surfaces are resistant to colloidal adsorption. Colloidal gold particles and flat gold substrates modified with SAMs form a convenient and versatile model system for examining existing theoretical models associated with the adsorption of colloids and proteins, and cellular attachment and adhesion at solid surfaces.

Introduction

Understanding the mechanism of protein adsorption and bacterial adhesion to synthetic surfaces is very important in the development of methods for eliminating or reducing biofouling of these surfaces in marine, biotechnological, medical, and industrial environments.[1–3] Self-assembled monolayers (SAMs) formed by the reaction of ω-substituted alkanethiols ($HS(CH_2)_nX$) with the surface of gold and other metals are versatile, well-defined structures that can be used to generate a wide range of surface chemistries.[4–6] The ease with which these SAMs can be used to obtain different interfacial chemistries (e.g., hydrophilic, hydrophobic, polar, or ionic properties) by variation of the terminal functional group, X, and by using mixed SAMs formed from different alkanethiols with different mole fractions, χ, makes them ideal candidates as model systems for the investigation of the interactions of macromolecules and cells with synthetic surfaces.[7,8] For example, model systems comprising SAMs formed from alkanethiols with a variety of terminal functional groups (e.g., OH, COOH, CF_3, CH_3, oligo(ethylene glycol)) have been reported for the study of protein adsorption and bacterial adhesion at solid–liquid interfaces.[9–11]

On the basis of these previous reports, we have designed a model system consisting of planar films and particles of gold, both modified by reaction with ω-substituted alkanethiols. Because SAMs can be used to form surfaces with controlled chemical composition, it is possible to precisely control the surface free energies of both the planar gold films and of the gold particles. The primary advantage of this model system for studying colloidal adsorption is that the surface free energy and size of the colloidal particles can be easily controlled and precisely varied over a wide range. This is a feature that is often impractical or impossible to achieve when investigating the adsorption of biological colloids.

We formed mixed SAMs from (1-mercaptoundec-11-yl)-hexa(ethylene glycol) ($HS(CH_2)_{11}(OCH_2CH_2)_6OH$, herein abbreviated as HSC11EG6) and 1-dodecanethiol (HS-$(CH_2)_{11}CH_3$, abbreviated as HSC12) in which the relative mole fraction of SC11EG6 in the planar SAMs (χ_{EG6}^{surf}) was varied from 0 to 1.0, in order to obtain films with different compositions and wettabilities. These were employed to study the interactions of two types of SAM-modified particles that varied in surface composition with planar surfaces. A method was developed to produce colloidal gold particles that vary systematically in surface properties on the basis of derivatization of their surfaces with mixtures of HSC11EG6 and HSC12. Our results suggest that this model system adequately simulates certain aspects of the adsorption of proteins and bacteria with synthetic surfaces.

Experimental Section

Materials. (1-Mercaptoundec-11-yl)hexa(ethylene glycol) was synthesized according to Pale-Grosdemange *et al.*[12] 1-Dodecanethiol, which was purified by chromatography on silica gel, citric acid trisodium salt dihydrate, and hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4\cdot3H_2O$) were all from Aldrich Chemical Co.

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Preparation of Gold Films. Glass slides were cleaned with acetone, ethanol, freshly-prepared piranha solution (a 7:3 v/v mixture of concentrated H_2SO_4 and 30% aqueous H_2O_2), and DI water in this sequence. (*Caution: piranha solution is a very strong oxidant and should be handled with extreme care.*) Planar gold films were then prepared by evaporative plating of chromium (10 Å) and then gold (200 Å) onto glass slides.

Synthesis of Colloidal Gold Particles (CAu). An aqueous solution of 0.2 mL 1% citric acid trisodium salt dihydrate was added to 200 mL of a boiling solution of 0.01% $HAuCl_4$ and refluxed for 15 min to give gold particles with diameter 90 nm.[13] Their concentration was 10^{12} particles/mL in water for all subsequent manipulations.

Preparation of Model Organic Surfaces. SAMs were formed by immersing two planar gold substrates (1 × 3 cm²) in a 1 mM ethanolic solution of HSC11EG6 and/or HSC12 for 24 h. The mole fraction of HSC11EG6 versus HSC12 in the solution was varied between 0 and 1.0 in order to obtain surfaces that varied in composition and in free energy. For each type of SAM investigated, one sample was used for XPS and contact angle experiments, while the other was used for studies of adsorption of colloidal gold particles. The colloidal particles were surface-modified by adding 0.05 mL of the ethanolic solution (1 mM) of mixed alkanethiols to 10 mL of the colloidal gold suspension, sonicating 15 min, and allowing to react overnight. The relative mole fractions to total thiols of HSC11EG6 in ethanol solution were 0.15 and 0.4.

Adsorption of Modified Gold Particles onto SAMs. Samples of SAM-modified gold films were placed in aqueous suspensions of SAM-modified gold colloids for 2 h. The films were then removed and rinsed with deionized water using a micropipet and dried in a stream of nitrogen. Scanning electron microscopy (SEM) was used to quantify the extent of colloidal adsorption to the planar SAMs. The numbers of gold particles per square micrometer (average ± standard deviation) were obtained by counting particles in three different areas.

Characterization. XPS spectra were acquired using a Physical Electronics 5400 ESCA system with monochromatized Al $K\alpha$ radiation and the detector at an angle of 45°, as described previously.[14] Binding energies in the spectra were referenced to the Au $4f_{7/2}$ peak at 84.0 eV. An estimate of the relative mole fraction of SC11EG6 in the mixed SAMs (χ_{EG6}^{surf}) was obtained by dividing the intensity of the O 1s X-ray photoelectron peak obtained from the mixed SAM by that of a SAM containing only the SC11EG6 component and by assuming that this normalized intensity is directly proportional to the number of oxygen atoms in the SAM.[9]

The advancing contact angles of water (θ_a) on planar SAMs were determined at ambient laboratory temperature (20–25 °C) with a contact angle goniometer (Ramé-Hart Model 100-00). The data are the average of three measurements taken at three different locations on the sample. A qualitative measure of the wettability of gold particles modified with SAMs was obtained as follows. An aliquot of the suspension of the SAM-modified colloidal gold was placed on a cleaned glass slide (or a cleaned silicon wafer), and the water was allowed to evaporate. After repeating this process several times to form a layer of the particles, the advancing contact angles were measured.

Results and Discussion

Figure 1 is a schematic diagram of our model system. The surfaces of the gold substrate and of the gold particles were modified with different mole fractions of HSC11EG6 and HSC12 to obtain organic surfaces and colloidal particles with a wide range of surface tensions. Several studies have examined the structure of SAMs formed by adsorption of ω-substituted alkanethiols on planar gold films[4–8] and on gold particles.[15,16] These studies suggest

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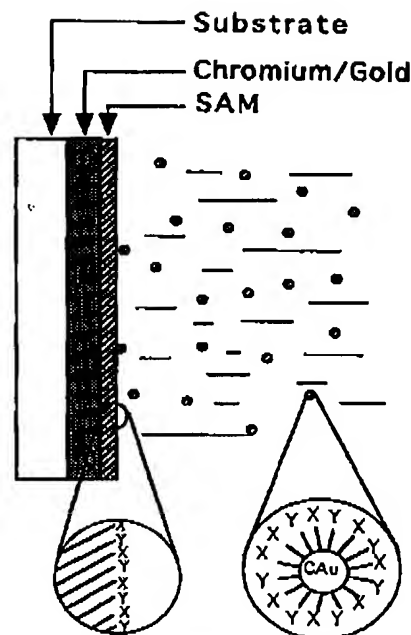(16) Weisbecker, C. S.; Merritt, M. V.; Whitesides, G. M. *Langmuir* 1996, *12*, 3763.

Figure 1. Schematic representation of the model system used for the study of adsorption of colloidal gold particles surface-modified with mixed SAMs onto the surface of planar films of mixed SAMs. The mixed SAMs are formed from $HS(CH_2)_{11}X$ (X = CH_3) and $HS(CH_2)_{11}Y$ (Y = $(OCH_2CH_2)_6OH$) and vary in mole fraction of $S(CH_2)_{11}(OCH_2CH_2)_6OH$ versus $S(CH_2)_{11}CH_3$. Features in the schematic are not drawn to scale.
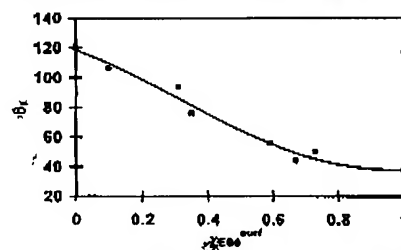
Figure 2. Wettability as a function of content of $HS(CH_2)_{11}$-$(OCH_2CH_2)_6OH$ in the SAM (χ_{EG6}^{surf}). The wettability of mixed SAMs, as measured by θ_a, the advancing contact angle of water on the SAMs, increases as a function of χ_{EG6}^{surf}. χ_{EG6}^{surf} was estimated from XPS. Each data point represents an average of three separate measurements.

that the terminal functional group of the substituted alkanethiol largely determines the interfacial properties of these monolayers.

The relationship between wettability and composition (χ_{EG6}^{surf}) of the mixed SAM is depicted in Figure 2. From this figure, it is clear that the hydrophobicity of the surface of the mixed SAMs decreases steadily as the content of EG6 is increased. As we describe below, the plot in Figure 2 is useful for predicting the tendency for adsorption of colloidal gold particles onto the mixed SAMs.

Figure 3 presents the relationship between the adsorption of modified colloidal gold particles and χ_{EG6}^{surf} of the planar SAMs.[17] From these data, it is apparent that the adsorption of the two kinds of particles with different

(17) Approximately 5.0 × 10^{14} end group sites/cm² on the planar SAMs can interact with the particles (see ref 6).

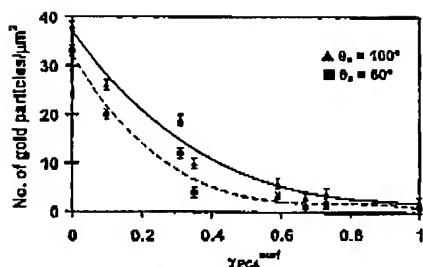**Figure 3.** Adsorption of colloidal gold (CAu) particles surface-modified with SAMs (θ_a = 100°, 60°) from water onto planar SAMs with different contents of SC11EG6. The initial concentration of CAu particles in the water suspensions was 10^{12} particles/mL. SAMs were exposed to a suspension of CAu for 2 h. The lines are meant only as a guide to the eye.

surface wettabilities decreases with increasing surface hydrophilicity (i.e., with increasing surface tension). These results are similar to those obtained for protein adsorption to mixed SAMs.[9] In addition, with increasing particle hydrophobicity (compare θ_a = 60° and θ_a = 100°), the extent of adsorption increases. Comparing the data in Figure 3 with those in Figure 2 suggests that, for our mixed monolayer system, SAMs with χ_{EG6}^{surf} that give rise to a θ_a of approximately 40° exhibit very low levels of colloidal adsorption. The data in Figure 3 thus suggest that the driving force for the adsorption of these modified colloidal particles onto organic surfaces in aqueous solution decreases as the surface tension of the organic surface increases and as the surface tension of particle increases. This is in agreement with the theoretical prediction of Absolom *et al.* for particles with surface tension lower than that of the medium they are suspended in (see below).

Several studies have reported that the adsorption of proteins and bacteria from aqueous solutions is determined to a large extent by thermodynamic considerations.[18-20] For example, Absolom *et al.* examined the adhesion of five strains of bacteria with different average surface free energy to various polymeric surfaces that varied in their surface free energy from liquid media that also varied systematically in surface free energy.[20] According to the formalism of Absolom *et al.*, the tendency for and the extent of adhesion of model bacteria or protein particles from a suspension onto a synthetic surface are determined by the surface properties of all three phases involved. Specifically the surface tensions of the adhering

particles (γ_{pv}), of the synthetic substrate (γ_{sv}), and of the suspending liquid medium (γ_{lv}) were postulated to control the adsorption phenomena. The driving force for adhesion was reported to decrease with increasing surface tension of the synthetic material (γ_{sv}) when the surface tension of the suspending medium is larger than that of the particles (i.e., $\gamma_{lv} > \gamma_{pv}$).

From this limited set of data, it is premature to conclude a detailed mechanism of adsorption of colloidal particles or to develop a theory of colloidal adsorption applicable to any organic surface. pH, ionic strength, and temperature of the suspension are likely to be other important factors that may affect the adsorption of colloidal particles. However, our results indicate that SAMs formed by ω-substituted alkanethiols onto gold substrates and gold particles provide a useful model system to study hypotheses related to both thermodynamic[18-20] and kinetic[21,22] aspects of colloidal adsorption and with which to investigate mechanisms of macromolecular adsorption and bacterial attachment.

Further studies will focus on designing experiments to test the other two cases in which adsorption may occur, i.e., when $\gamma_{lv} < \gamma_{pv}$ and $\gamma_{lv} = \gamma_{pv}$ in aqueous suspension, and investigating the effects of pH, ionic strength, temperature, and size of colloidal gold particles on the adsorption of colloidal particles.

Conclusions

Data obtained by adsorption of colloidal gold particles onto SAMs indicate that adsorption of colloidal particles onto organic surfaces, from aqueous suspensions, follows thermodynamic predictions to a considerable extent: more colloidal particles adsorb to more hydrophobic organic surfaces when the surface tension of the suspension is greater than that of the colloidal particles. SAM-modified gold films and colloidal gold particles provide a good model system for the study of adsorption of colloidal particles onto organic surfaces. This model system can be used to be simulate several properties of adsorption phenomena of biological colloidals, such as tendency for adsorption. Other properties of biological systems (e.g. spreading of proteins and cells after adsorption) are beyond the simulation capability of this model system.

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